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EP-A-0 002 899
EP-A-0 002 900
DE-A-2 704 039
DE-B-1 960 361
FR-A-2 228 721
GB-A-1 365 318
GB-A-1 484 495
GB-A-1 553 209
GB-A-1 567 948
GB-A-2 018 232
NL-A-7 512 645
US-A-3 308 069
US-A-3 644 200

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(56) References cited:

US-A-3 702 886
US-A-4 175 114

Nature Vol. 280 23.8.79 pages 664/5 Bibby et al.
J. Chem. Soc. (1961) pages 971 to 982, Barrer & Denny

Chem. Abs. Vol. 69 no. 108573c (1968)

Chemistry Letters (1984) pages 1055 to 1058

Ind. Eng. Chem. Prod. Res. Dev. (1983) Vol. 22 pages 22-60

Courier Press, Leamington Spa, England.

(56) References cited:

American Minerologist Vol. 65 (1980) pages 1012 to 1019

Zeolites Vol. 4 (1984) page 283

Description

The present invention relates generally to an improved process for the production of crystalline aluminosilicates and to the use of the crystalline aluminosilicates produced thereby as conversion catalysts and catalyst supports.

Crystalline aluminosilicates, both natural and synthetic, have been shown to contain a wide variety of positive ions. These aluminosilicates have skeletal structures which are made up of three dimensional networks of SiO_4 and AlO_4 tetrahedra, corner-linked to each other by shared oxygen atoms. There are no unshared oxygen atoms in the anionic framework so that the ratio of the total aluminium and silicon atoms (Al + Si) to oxygen atoms is 1:2 and the negative charges created by the replacement of Si (IV) atoms by Al (III) atoms are neutralised by an electrochemical equivalent of cations. Those cations in the initially formed aluminosilicate are generally alkali metal cations. Until recently it was not possible to synthesise crystalline aluminosilicates having a silica to alumina molar ratio greater than 10:1. However, this has recently been achieved and there has resulted a range of crystalline aluminosilicates having a higher silica to alumina ratio, high stability, extremely high acidity, and the ability to catalyse many kinds of conversion reactions, in particular the conversion of aliphatic compounds into aromatic compounds. This was achieved by the use in the preparation of the aluminosilicate of one or more quaternary alkylammonium compounds such as tetramethylammonium, tetraethylammonium, tetrapropylammonium, and tetrabutylammonium compounds. By employing such large cations crystalline aluminosilicates having a silica to alumina ratio greater tha 100:1 can be produced. However, the use of quaternary alkylammonium compounds is not without its disadvantages, not the least of which is their relatively high cost. British Patent Specification No. 1365318 discloses an attempt to overcome this disadvantage by employing in the synthesis the precursors of the tetraalkylammonium compound, i.e. $R_1R_2R_3N + R_4X$ in which R_1, R_2 and R_3 are selected from aryl, substituted aryl, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl and hydrogen, R_4 is alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, aryl and substituted aryl and *x* is an electronegative group. In a special embodiment of the invention the compound $R_1R_2R_3N$ may be used in the absence of R_4X provides that the compound $R_1R_2R_4N$ is used. This method only partially alleviates the expense problem and does not eliminate a further disadvantage associated with crystalline aluminosilicates prepared from tetraalkylammonium compounds, namely that in order to exchange an ammonium or other cation into the zeolite preliminary to producing the active form of the catalyst it is necessary to calcine the zeolite.

British Patent Specification No. 1484495 describes a zeolite designated KS07 characterised by its X-ray powder diffraction, its composition expressed in mol of oxides as $0.7—1.3\ Na_2O.Al_2O_3.3.5—7.5\ SiO_2 0.01—2\ MO_n/_2.0—12\ H_2O$ and its n-hexane sorption characteristics, which zeolite is prepared by crystallisation at a temperature between 70 and 160°C from an aqueous mixture containing one or more compounds of each of sodium, aluminium, silicon and at least one metal of Group VIII of the Periodic System of Elements, the Group VIII compound or each of the Group VIII metal compounds being a cationic complex having the general formula $[M(X)_a(Y)_b]^{n-b}$ wherein M = a Group VIII metal, X = NH_3 or an amine, Y = halogen, n = the valency of the metal M, varying between 1 and 6, a = 2—6, b = 0—5 and n−b is greater than or equal to +1, the aqueous starting mixture having the composition, expressed in mol of oxides $2—10\ Na_2O.AL_2O_3.\ 8—20\ SiO_2 0.01—2.5\ MO_n/_2.100—450\ H_2O$.

Recent attempts to overcome the aforesaid disadvantages are described in British Patent Specification No: 1553209 and UK Patent Application No: 2018232A. British Patent Specification No: 1553209 describes a method of making such a zeolite by reacting an aqueous mixture comprising at least one silica source, at least one alumina source, at least one alkali not including ammonium or phosphonium compounds, and at least one alcohol, the mixture having the composition:

SiO_2/Al_2O_3	20 to 200
$OH(R)/Al_2O_3$	0.02 to 0.25
M_2O/SiO_2	10 to 1000
H_2O/M_2O	1 to 100

where M is one or more of lithium, sodium or potassium;

M_2O refers to free alkali; and

OH(R) is a hydroxy group present as an alcohol.

GB Patent Application No: 2018232 describes and claims a process for the preparation of crystalline aluminosilicate zeolites having a SiO_2/Al_2O_3 molar ratio of at least 12 and a constraint index between 1 and 12, characterised in that an aqueous mixture containing the following compounds:

one or more compounds of an alkali and/or an alkaline earth metal, (M)

one or more Al compounds,

one or more Si-compounds,

one or more alcohols (ROH), and

ammonia, in which mixture the various compounds are present in the following molar ratios expressed — with the exception of the alcohols and ammonia — in moles of the oxides:

$SiO_2 : Al_2O_3 \geqslant 12:1$

$(M)_{2/n}O : SiO_2 = 0.01—1.0$

$H_2O : (M)_{2/n}O = 10—500$

$ROH : Al_2O_3 = 5—500$, and

$ROH : NH_3 > 2$

(n is the valency of M)

is maintained at elevated temperature until the zeolite has been formed and in that subsequently the crystals of the zeolite are separated from the mother liquor.

US—A—4,175,114 discloses a method of synthesising a crystalline ZSM—5 aluminosilicate in the absence of an organic template but employing (1) ZSM—5 seeds, (2) mixtures of ZSM—5 seeds and alcohol, (3) mixtures of ZSM—5 seeds with alcohol and ammonium hydroxide and (4) mixtures of ZSM—5 seeds with ammonium hydroxide. It does not suggest using ammonium hydroxide in the absence of seeds.

DE—A—2,704,039 also discloses the preparation of high silica zeolites in the absence of an organic template involving the use of inorganic components. It does not, however, disclose the use of ammonia in the preparation.

Our own published European Application Nos: 78300773.5 (BP Case 4509) and 78300774.3 (BP Case 4509/4625) (Publication Numbers EP—A—0,002,899 and EP—A—0,002,900 respectively) describe the use of mono-, di- and trialkanolamines as organic nitrogen bases in the production of crystalline aluminosilicates. A particular advantage of their use is that the precursors of such alkanolamines in the form of an alkylene oxide and ammonia may be used in place of the preformed alkanolamine, thereby reducing the cost relative to quaternary alkylammonium compounds significantly.

We have now unexpectedly found that crystalline aluminosilicates having a silica to alumina molar ratio greater than 12:1 can be produced from an ammonia-containing mixture in the absence of an alcohol or an alkylene oxide. Crystalline aluminosilicates so-produced do not require calcination prior to ion-exchange.

Accordingly, the present invention provides a process for the production of a crystalline aluminosilicate zeolite having a silica to alumina molar ratio greater than 12:1 by mixing a source of silica, a source of alumina, a source of alkali metal, water and a source of ammonium ions, and maintaining the mixture at elevated temperature for a time such that crystallisation occurs characterised in that a source of ammonium ions is employed in the absence of an alcohol and alkylene oxide, quaternary ammonium compounds and their precursors, and a seed and the source of silica, the source of alumina, the source of alkali metal, water and the source of ammonium ions are mixed in the molar proportions (expressed in the case of the silica and alumina sources in terms of the equivalent moles of the oxide, in the case of the alkali metal source in terms of the equivalent moles of the hydroxide [MOH] and in the case of the source of ammonium ions in terms of free ammonia):

$SiO_2 : Al_2O_3$ greater than 12:1

$MOH : Al_2O_3$ in the range from 1:1 to 20:1

$SiO_2 : NH_3$ in the range from 1:1 to 200:1, and

$H_2O : MOH$ in the range from 30:1 to 300:1.

Suitable sources of silica include, for example, sodium silicate, silica hydrosol, silica gel, silica sol and silicic acid. The preferred source of silica is an aqueous colloidal dispersion of silica particles. A suitable commercially available source of silica is LUDOX Colloidal Silica manufactured by Du Pont (LUDOX is a Registered Trade Mark).

Suitable sources of alkali metal include alkali metal hydroxides and alkali metal oxides. Preferably the alkali metal is sodium.

The source of ammonium ions may be for example ammonium hydroxide or an ammonium salt such as the halide, nitrate, sulphate or carbonate. Ammonium hydroxide may be added as an aqueous solution or formed 'in situ' by passing ammonia gas into the aqueous mixture. 35% w/w and 25% w/w aqueous ammonia solutions having densities of 0.880 g/ml and 0.910 g/ml respectively at 20°C are commercially available and may be used in the process of the invention, but aqueous solutions of other concentrations may also be used.

It will be appreciated that each source of silica, alumina, alkali metal and ammonium ion can be supplied by one or more initial reactants and then mixed together in any order. For example, sodium silicate is a source of both sodium and silica and an aluminosilicate is a source of both alumina and silica. Thus the source of alumina and the source of silica may be supplied in whole or in part by an aluminosilicate, which may be either crystalline or amorphous. A seed, that is a small portion of the desired crystalline product, may be introduced if so desired but it is an advantage of the present invention that the introduction of a seed is not necessary for the efficient performance of the invention.

The molar composition of the initial mixture is preferably as follows:

SiO_2 : Al_2O_3 in the range from 20:1 to 50:1

MOH : Al_2O_3 in the range from 2:1 to 10:1

SiO_2 : NH_3 in the range from 20:1 to 100:1

H_2O : MOH in the range from 30:1 to 100:1.

Even more preferably the molar composition of the initial mixture is as follows:

SiO_2 : Al_2O_3 in the range from 25:1 to 45:1

MOH : Al_2O_3 in the range from 3:1 to 7:1

SiO_2 : NH_3 in the range from 25:1 to 40:1

H_2O : MOH in the range from 40:1 to 60:1.

Conditions which effect the formation of the crystalline aluminosilicate may be, for example, a temperature in the range from 120 to 210°C, preferably from 135 to 190°C and a pressure in the range from autogenous to 26 bar (400 psig), preferably from autogenous to 16 bar (250 psig). Suitably the pressure may be autogenous, that is the pressure generated within a closed vessel at the crystallisation temperature. Alternatively pressures within the aforesaid ranges above autogenous pressure may be employed. Pressures above autogenous pressure may be achieved for example by pressurising with a suitable gas, e.g. nitrogen. The mixture may suitably be maintained under these conditions for a time of at least 4 hours and preferably from 20 to 150 hours. Generally a time of about 48 hours will be found suitable though times up to and in excess of 7 days may be employed. Of course the time should not be so protracted that the crystalline aluminosilicate produced is converted to quartz.

The reaction is suitably carried out in a closed vessel capable of withstanding the elevated pressure employed during the process. Furthermore the reaction mixture may be agitated during the formation of the aluminosilicate. The solid aluminosilicate so-prepared may be recovered, e.g. by filtration and washed, suitably with water at a temperature in the range, for example, of from 15 to 95°C.

Crystalline aluminosilicates prepared by the process of the present invention may be used as catalysts or as catalyst supports. The crystalline aluminosilicate may be used on its own or admixed with up to 80% by weight of another support material such as silica or alumina.

Crystalline aluminosilicates prepared in the manner of the present invention will invariably contain alkali metals, which are generally undesireable if the aluminosilicate is to be used for catalytic purposes. Thus it is preferred to reduce the alkali metal content of the aluminosilicate to less than 0.2% by weight, or for certain catalytic applications, such as in the dehydrocyclo-dimerisation of paraffins to less than 0.02% by weight. This may be achieved by subjecting the aluminosilicate to one or more ion exchanges with a solution containing suitable cations. For example, the aluminosilicate may be ion-exchanged with a solution containing ammonium cations and thereafter calcined to produce the active hydrogen-form of the aluminosilicate. Before ion-exchange it may be preferable to treat the aluminosilicate with a solution of an acid, e.g. an aqueous mineral acid.

For catalytic purposes it is preferred to active the aluminosilicate before use, suitably by heating in air at a temperature in the range 400 to 700°C for a period of from 2 to 48 hours.

Further there may be incorporated into the crystalline aluminosilicate one or more metals belonging to Groups IB, IIB, IIIA, IVA, VA or VIII of the Periodic Table of the elements as published by the Chemical Rubber Publishing Company. Suitable metals include copper, silver, zinc, gallium, indium, thallium, lead, antimony, bismuth, iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium and platinum. The amount of the metal or metals incorporated may be in the range from 0.1 to 5.0% by weight based on the weight of the aluminosilicate. The metal or metals may suitably be incorporated by impregnation with a suitable compound or compounds. The compounds of the metals used are suitably those compounds which will decompose on heating to form the corresponding oxides and which are soluble in water, e.g. the nitrates or chlorides. The aluminosilicate may thus be impregnated with an aqueous solution of a compound of the desired metal and the impregnated mass thereafter calcined to produce the metal oxide 'in situ' deposited in the interstices of the aluminosilicate structure. Alternatively, or in addition, the metal or metals may be incorporated by ion-exchange. A suitable method for preparing a gallium-exchanged crystalline aluminosilicate catalyst comprises washing the crystalline aluminosilicate with acidified and/or deionised water, calcining the washed product at an elevated temperature, contacting the calcined product with an acid, refluxing the acid-treated product with a solution of a gallium compound to produce a gallium-exchanged aluminosilicate and washing the gallium-exchanged aluminosilicate with water to render it substantially free from any impregnated gallium or gallium compound.

In a further embodiment of the invention the aluminosilicate employed additionally contains one or more non-metallic elements belonging to Groups IIIA and VA of the Periodic Table, especially boron and phosphorus. The non-metallic element may be incorporated into the aluminosilicate by treatment with a suitable compound containing the non-metallic element, e.g. phosphoric acid, trimethylphosphite or phosphorus trichloride, followed by heating. The amount of the non-metallic element present in the impregnated aluminosilicate preferably ranges from 0.1 to 5.0% by weight.

The crystalline aluminosilicates so-prepared, with or without the hereinbefore described treatments and/or modifications, may be used as catalysts in the form of a fixed or a fluidised bed in aromatisation, disproportionation, cracking, alkylation, dehydrocyclodimerisation, oligomerisation, isomerisation and hydrogenation reactions. Additionally the aluminosilicates may be used as catalysts in the dehydration of alcohols and ethers.

The following Examples are given for the purpose of illustrating the invention.

In the Examples reference will be made to Ludox Type LS30 silica sol and Ludox Type AS40 silica sol. Type LS30 silica sol contains sodium ions as the stabilising counter ions and has a titratable alkali content of 0.1% wt/wt calculated as Na_2O. Type AS40 silica sol contains ammonium ions as the stabilising counter ions and has a silica to ammonia ratio (i.e. $SiO_2:NH_3$) of 80:1 molar.

Example 1

(a) Preparation of crystalline aluminosilicate

Alumina, Laporte Type A (0.89 g) was dissolved in a solution of sodium hydroxide (1.75 g) in deionised water (12.5 ml) by warming. This solution was then added with vigorous stirring to Ludox Type LS30 silica sol (52.5 g, containing 30% wt/wt silica) and 0.910 aqueous ammonia solution (0.6 ml, containing 25% wt/wt ammonia). The mixture was stirred for three hours and then placed in an agitated, glass-lined pressure vessel and heated at 170°C for 48 hours. The solid crystalline product was filtered off.

(b) Preparation of active form of crystalline aluminosilicate

The crystalline product recovered from (a) above was ion-exchanged by refluxing with one molar ammonium chloride solution (250 ml). This operation was repeated twice. The mixture was filtered and the solid washed with deionised water (250 ml) and dried at 120°C for 16 hours. A sample of the solid was calcined by heating at 500°C and the calcined sample analysed by X-ray fluorescence. It was shown to contain 43% w/w silicon, 1.93% w/w aluminium and less than 0.01% w/w sodium. The analysis corresponds to a silica to alumina molar ratio of 45:1. The X-ray diffraction pattern (XRD) of the calcined crystalline aluminosilicate was determined by standard techniques using as radiation the K-alpha doublet of copper. The pattern expressed in terms of 2-theta, d(Angstroms) and I/Io is given in Table 1. The XRD pattern is characteristic of an MFI-type zeolite as defined in the Atlas of Zeolite Structure Types by W. M. Meier and D. H. Olson, published by the Structure Commission of the International Zeolite Association, 1978.

10 g of the uncalcined aluminosilicate prepared as described above was crushed to powder and mixed with 10 g Ludox silica sol (containing 30% wt/wt silica). The suspension was evaporated to dryness on a steam-bath and finally dried at 120°C. The solid was then broken down to form 5 to 16 mesh (BSS) (3.353 to 1.003 mm respectively openings) granules and calcined at 500°C for 16 hours in air.

Example 2

(a) Preparation of crystalline aluminosilicate

Alumina, Laporte Type A (13.35 g) was dissolved in a solution of sodium hydroxide (26.25 g) in deionised water (187.5 ml) by warming. This solution was then added with stirring to Ludox silica sol Grade AS40 (590 g, containing 40% wt/wt silica) and 0.910 aqueous ammonia solution (9.0 ml, containing 25% wt/wt ammonia). The pH of the mixture was 13.1.

1.5 g of the active form of the crystalline aluminosilicate prepared as described in Example 1 was added and the whole was placed in a rocking stainless steel autoclave and heated at 170°C for 64 hours. The crystalline aluminosilicate product was filtered off. It had a silica to alumina molar ratio of greater than 12:1 and to an X-ray diffraction pattern after calcination, substantially the same as shown in Table 1.

(b) Preparation of active form of crystalline aluminosilicate

The solid product from (a) was ion-exchanged by refluxing with one molar ammonium chloride solution (500 ml). This operation was repeated twice. The mixture was filtered and the solid washed with deionised water (1000 ml) and dried at 120°C for 16 hours. The solid was then broken to form 5 to 16 mesh (BSS) (3.353 to 1.003 mm respectively openings) granules and calcined at 500°C for 16 hours in air.

Example 3

8.0 g of the granules of the activated crystalline aluminosilicate prepared as described in Example 1 were mixed with an aqueous gallium nitrate solution (6 ml, containing 0.05 g gallium/ml) and the whole evaporated to dryness on a steam-bath. The solid was dried at 120°C for 16 hours and activated by heating in air at 500°C for 16 hours.

Example 4

Alumina, Laporte Type A (0.89 g) was dissolved in a solution of sodium hydroxide (1.75 g) in deionised water (12.5 ml) by warming. This solution was then added with vigorous stirring to a mixture of Ludox silica sol, Type AS40 (39.4 g, containing 40% wt/wt silica) and deionised water (13.1 ml). The suspension was stirred for three hours and then placed in an agitated glass-lined pressure vessel and heated at 170°C for 64 hours.

The solid product was filtered off. It had a silica to alumina molar ratio of greater than 12:1 and an X-ray diffraction pattern, after calcination, substantially the same as that shown in Table 1. The product was processed as described in Example 1(b).

Testing of Crystalline Aluminosilicates as Catalysts

Example 5

The activity of the activated aluminosilicate prepared as described in Example 1 was tested by passing a gaseous feed of methanol over the catalyst in a glass reactor at 400°C and 3.2 seconds contact time.

Of the methanol fed, 2% (molar) was converted to C_2, 27% to C_3 and 30% to C_4 hydrocarbons and the remainder was a complex mixture of straight- and branched-chain hydrocarbons and aromatics. The methanol conversion was 100%.

Example 6

The activity of the activated aluminosilicate prepared as described in Example 1 was tested by passing a gaseous feed of a C_3 hydrocarbon mixture (78.1% propane, 19.1% propylene and 2.8% ethane) over the catalyst in a heated glass reactor. The conditions used and the results obtained therefrom are given in the following Table 2.

Example 7

The activity of the activated aluminosilicate prepared as described in Example 2 was tested as described in Example 6. The conditions used and the results obtained therefrom are given in the following Table 2.

Example 8

The activity of the activated catalyst prepared as described in Example 3 was tested as described in Example 6. The conditions used and the results obtained therefrom are given in the following Table 2.

Example 9

The activity of the activated catalyst prepared as described in Example 4 was tested in the manner described in Example 6. The conditions used and the results obtained therefrom are given in the following Table 2.

TABLE 1
X-Ray Diffraction Data for Aluminosilicates after Calcination at 500°C/for 6 hours.

2-Theta	d-(Angstrom)	I/I_0
4.96	17.823	4
5.11	17.312	5
5.14	17.181	5
7.09	12.462	6
7.96	11.104	100
8.87	9.973	55
9.11	9.713	17
11.94	7.416	5
13.23	6.693	7
13.96	6.344	11
13.83	5.976	14
15.56	5.695	10
15.94	5.560	12
16.67	5.319	5
17.70	5.013	5
17.85	4.971	6
19.29	4.603	6
20.38	4.358	9
20.89	4.253	11
22.25	3.996	6
23.14	3.844	89
23.35	3.811	64
23.79	3.741	34
23.95	3.716	42
24.45	3.641	29
24.81	3.590	4
25.64	3.475	8
25.94	3.435	13
26.28	3.391	11
26.67	3.343	9

TABLE 1 (continued)

2-Theta	d-(Angstrom)	I/I_0
26.97	3.307	10
27.44	3.251	4
29.33	3.046	10
29.96	2.983	11
30.08	2.971	11
30.39	2.941	6
32.80	2.731	4

TABLE 2

Test	Hours on stream	Reaction temperature °C	Contact time sec	$C_3^{2.}$ Conversion %	Molar Yields 3%				Selectivity to Aromatics	Composition of aromatics %		
					CH_4	C_2H_4	C_2H_6	Aromatics		Benzene	Toluene	Xylene
Ex. 6	2	450	16.5	22.7	5.5	0.7	4.6	11.9	52.4	17	37	21
	2	500	16.6	57.9	13.4	1.4	11.4	31.2	53.9	26	42	19
	2	550	16.3	85.3	20.5	3.1	11.0	50.7	59.4	33	37	12
	2	550	6.2	52.2	13.6	5.0	9.2	24.4	46.7	21	42	21
Ex. 7	2	450	16.9	19.5	2.4	0.5	2.4	16.6	85.1	19	47	30
	2	500	17.6	35.5	8.6	1.3	7.4	18.2	51.3	18	35	20
	2	550	17.1	67.8	17.0	3.2	10.4	37.2	54.9	24	39	17
	2	550	5.9	30.1	9.3	4.8	6.4	9.6	31.9	19	41	27
Ex. 8	1	550	18.0	95.4	13.6	0.7	11.0	70.2	73.6	34	34	10
	1	550	6.1	67.6	8.6	0.1	5.2	51.7	76.5	32	44	15
Ex. 9	1	550	18.0	86.9	16.3	2.5	8.6	59.7	68.7	30	38	14

In the above Examples and Table 2:

1. Contact time $= \frac{\text{Volume of catalyst in mls}}{\text{Total volume of gas (in mls/sec at NTP)}}$

2. C_3 Conversion $= \frac{\text{Moles of } C_3 \text{ hydrocarbon consumed}}{\text{Moles of } C_3 \text{ hydrocarbon fed}} \times 100$

3. Molar Yield $= \frac{\text{Moles of } C_3 \text{ hydrocarbon converted to particular product}}{\text{Moles of } C_3 \text{ hydrocarbon fed}} \times 100$

4. Selectivity $= \frac{\text{Moles of } C_3 \text{ hydrocarbon converted to aromatics}}{\text{Moles of } C_3 \text{ hydrocarbon consumed}} \times 100$

Claims

1. A process for the production of a crystalline aluminosilicate zeolite having a silica to alumina molar ratio greater than 12:1 by mixing a source of silica, a source of alumina, a source of alkali metal, water and a source of ammonium ions, and maintaining the mixture at elevated temperature for a period such that crystallisation occurs characterised in that a source of ammonium ions is employed in the absence of an alcohol, an alkylene oxide, quaternary ammonium compounds and their precursors, and a seed and the source of silica, the source of alumina, the source of alkali metal, water and the source of ammonium ions are mixed in the molar proportions (expressed in the case of the silica and alumina sources in terms of the equivalent moles of the oxide, in the case of the alkali metal source in terms of the equivalent moles of the hydroxide [MOH] and in the case of the source of ammonium ions in terms of free ammonia):

SiO_2 : Al_2O_3 greater than 12:1

MOH : Al_2O_3 in the range from 1:1 to 20:1

SiO_2 : NH_3 in the range from 1:1 to 200:1, and

H_2O : MOH in the range from 30:1 to 300:1.

2. A process according to claim 1 wherein the source of ammonium ions is ammonium hydroxide.
3. A process according to claim 2 wherein the ammonium hydroxide is added as an aqueous solution.
4. A process according to claim 2 wherein the ammonium hydroxide is formed 'in situ' by passing ammonia gas into the aqueous mixture.
5. A process according to claim 1 wherein the source of ammonium ions is an ammonium salt.
6. A process according to any one of the preceding claims wherein the molar composition of the initial mixture is:

SiO_2 : Al_2O_3 in the range from 20:1 to 50:1

MOH : Al_2O_3 in the range from 2:1 to 10:1

SiO_2 : NH_3 in the range from 20:1 to 100:1

H_2O : MOH in the range from 30:1 to 100:1.

7. A process according to claim 6 wherein the molar composition of the initial mixture is:

SiO_2 : Al_2O_3 in the range from 25:1 to 45:1

MOH : Al_2O_3 in the range from 3:1 to 7:1

SiO_2 : NH_3 in the range from 25:1 to 40:1

H_2O : MOH in the range from 40:1 to 60:1.

8. A process according to any one of the preceding claims wherein the temperature is in the range from 120 to 210°C.
9. A process according to any one of the preceding claims wherein the alkali metal content of the crystalline aluminosilicate is reduced to less than 0.2% by weight.
10. A process according to claim 9 wherein the alkali metal content is reduced by ion-exchanging the

aluminosilicate with a solution containing ammonium cations to form the ammonium-exchanged aluminosilicate.

11. A process according to claim 10 wherein the ammonium-exchanged crystalline aluminosilicate is calcined to form the active hydrogen-form.

12. A process according to any one of the previous claims wherein there is incorporated into the crystalline aluminosilicate, either by ion-exchange or by impregnation or by both, one or more of the metals copper, silver, zinc, gallium, indium, thallium, lead, antimony, bismuth, iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium and platinum.

13. A process according to claim 12 wherein the metal is gallium.

14. A process according to any one of the preceding claims wherein there is incorporated into the crystalline aluminosilicate either boron or phosphorus.

Patentansprüche

1. Verfahren zur Herstellung eines kirstallinen Aluminosilikates mit einem molaren Verhältnis von Kieselsäure zu Tonerde größer als 12:1 durch Mischen einer Kieselsäurequelle, einer Tonerdequelle, einer Alkalimetallquelle, Wasser und einer Quelle für Ammoniumionen und Halten der Mischung auf erhöhter Temperatur für eine solche Dauer, daß die Kristallisation erfolgt, dadurch gekennzeichnet, daß eine Quelle für Ammoniumionen in Abwesenheit eines Alkohols, eines Alkylenoxids, quaternärer Ammoniumverbindungen und ihrer Vorläufer und eines Kristallisationskeims verwendet wird und die Kieselsäurequelle, die Tonerdequelle, die Alkalimetallquelle, Wasser und die Quelle für Ammoniumionen in den molaren Verhältnissen (ausgedrückt im Fall der Kieselsäure- und Tonerdequellen in Äquivalentmol des Oxids, im Fall der Alkalimetallquelle in Äquivalentmol des Hydroxids [MOH] und im Fall der Quelle für Ammoniumionen als freier Ammoniak):

SiO_2 : Al_2O_3 größer als 12:1

MOH : Al_2O_3 im Bereich von 1:1 bis 20:1

SiO_2 : NH_3 im Bereich von 1:1 bis 200:1 und

H_2O : MOH im Bereich von 30:1 bis 300:1.

2. Verfahren nach Anspruch 1, in welchem die Ammoniumionenquelle Ammoniumhydroxid ist.

3. Verfahren nach Anspruch 2, in welchem das Ammoniumhydroxid als eine wässrige Lösung zugefügt wird.

4. Verfahren nach Anspruch 2, in welchem das Ammoniumhydroxid in situ gebildet wird, indem man gasförmigen Ammoniak in die wässrige Mischung einleitet.

5. Verfahren nach Anspruch 1, in welchem die Ammoniumionenquelle ein Ammoniumsalz ist.

6. Verfahren nach einem der vorhergehenden Ansprüche, in welchem die molare Zusammensetzung der Anfangsmischung

SiO_2 : Al_2O_3 im Bereich von 20:1 bis 50:1

MOH : Al_2O_3 im Bereich von 3:1 bis 7:1

SiO_2 : NH_3 im Bereich von 20:1 bis 100:1

H_2O : MOH im Bereich von 30:1 bis 100:1 ist.

7. Verfahren nach Anspruch 6, in welchem die molare Zusammensetzung der Anfangsmischung

SiO_2 : Al_2O_3 im Bereich von 25:1 bis 45:1

MOH : Al_2O_3 im Bereich von 3:1 bis 7:1

SiO_2 : NH_3 im Bereich von 25:1 bis 40:1

H_2O : MOH im Bereich von 40:1 bis 60:1 ist.

8. Verfahren nach einem der vorhergehenden Ansprüche, in welchem die Temperatur im Bereich von 120 bis 210°C liegt.

9. Verfahren nach einem der vorhergehenden Ansprüche, in welchem der Alkalimetallgehalt des kristallinen Aluminosilikates auf weniger als 0,2 Gew.-% verringert wird.

10. Verfahren nach Anspruch 9, in welchem der Alkalimetallgehalt durch Ionenaustausch des Alumino-

silikates mit einer Ammoniumkationen enthaltenden Lösung zur Bildung des ammonium-ausgetauschten Aluminosilikates verringert wird.

11. Verfahren nach Anspruch 10, in welchem das ammoniumausgetauschte kristalline Aluminosilikat zur Bildung der aktiven Wasserstofform calciniert wird

12. Verfahren nach einem der vorhergehenden Ansprüche, in welchem in das kirstalline Aluminosilikat durch Ionenaustausch oder Imprägnierung oder beides ein oder mehrere der Metalle Kupfer, Silber, Zink, Gallium, Indium, Thallium, Blei, Antimon, Wismut, Eisen, Kobalt, Nickel, Ruthenium, Rhodium, Palladium, Iridium und Platin einverleibt werden.

13. Verfahren nach Anspruch 12, in welchem das Metall Gallium ist.

14. Verfahren nach einem der vorhergehenden Ansprüche, in welchem in das kristalline Aluminosilikat entweder Bor oder Phosphor einverleibt wird.

Revendications

1. Procédé de production d'une zéolite sous forme d'un aluminosilicate cristallin ayant un rapport molaire silice/alumine supérieur à 12/1, par mélange d'une source de silice, d'une source d'alumine, d'une source d'un métal alcalin, d'eau et d'une source d'ions ammonium, et par maintien du mélange à température élevée pendant une période telle que la cristallisation se produit, caractérisé en ce que

une source d'ions ammonium est utilisée en l'absence d'un alcool, d'un oxyde d'alkylène, de composés d'ammonium quaternaire et de leurs précurseurs, et d'un germe, et la source de silice, la source d'alumine, la source d'un métal alcalin, l'eau et la source d'ions ammonium sont mélangées dans les proportions molaires suivantes (exprimées, dans le cas des sources de silice et d'alumine, en équivalents molaires de l'oxyde, dans le cas de la source de métal alcalin, en équivalents molaires de l'hydroxyde [MOH] et, dans le cas de la source d'ions ammonium, en ammoniac libre):

SiO_2 / Al_2O_3 supérieur à 12/1

MOH / Al_2O_3 dans la plage de 1/1 à 20/1

SiO_2 / NH_3 dans la plage de 1/1 à 200/1, et

H_2O / MOH dans la plage de 30/1 à 300/1.

2. Procédé selon la revendication 1, caractérisé en ce que la source d'ions ammonium est l'hydroxyde d'ammonium.

3. Procédé selon la revendication 2, caractérisé en ce que l'hydroxyde d'ammonium est ajouté sous forme d'une solution aqueuse.

4. Procédé selon la revendication 2, caractérisé en ce que l'hydroxyde d'ammonium est formé in situ par circulation d'ammoniac gazeux dans le mélange aqueux.

5. Procédé selon la revendication 1, caractérisé en ce que la source d'ions ammonium est un sel d'ammonium.

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la composition molaire du mélange initial a les proportions suivantes:

SiO_2 / Al_2O_3 dans la plage de 20/1 à 50/1

MOH / Al_2O_3 dans la plage de 2/1 à 10/1

SiO_2 / NH_3 dans la plage de 20/1 à 100/1

H_2O / MOH dans la plage de 30/1 à 100/1.

7. Procédé selon la revendication 6, caractérisé en ce que la composition molaire du mélange initial a les proportions suivantes:

SiO_2 / Al_2O_3 dans la plage de 25/1 à 45/1

MOH / Al_2O_3 dans la plage de 3/1 à 7/1

SiO_2 / NH_3 dans la plage de 25/1 à 40/1

H_2O / MOH dans la plage de 40/1 à 60/1.

8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la température est comprise entre 120 et 210°C.

9. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la teneur en métal alcalin de l'aluminosilicate cristallin est réduite à moins de 0,2% en poids.

10. Procédé selon la revendicaiton 10, caractérisé en ce que la teneur en métal alcalin est réduite par échange d'ions de l'aluminosilicate avec une solution contenant des cations ammonium afin qu'il se forme l'aluminosilicate ayant subi un échange d'ions ammonium.

11. Procédé selon la revendication 11, caractérisé en ce que l'aluminosilicate cristallin ayant subi l'échange d'ions ammonium est calciné afin qu'il prenne la forme à hydrogène actif.

12. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce qu'un ou plusieurs des métaux cuivre, argent, zinc, gallium, indium, thallium, plomb, antimoine, bismuth, fer, cobalt, nickel, ruthénium, rhodium, palladium, iridium et platine sont incorporés dans l'aluminosilicate cristallin soit par échange d'ions soit par imprégnation, soit par ces deux opérations.

13. Procédé selon la revendication 12, caractérisé en ce que le métal est le gallium.

14. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que du bore ou du phosphore est incorporé à l'aluminosilicate cristallin.